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A METHOD FOR PRODUCING ACETOL

The invention concerns a method for producing acetol by dehydration of glycerol at higher temperatures.

Acetol, or hydroxyacetone, is used, among other ways, as a reducing agent in dyeing with vat dyes (the periodical "Textil Praxis International" 1989, p. 737). It is also used as a starting material for heterocycle synthesis and can be used, for example, for enzymatic preparation of R-(-)-1,2-propanediol (DE 38 30 253 A1).

On an industrial scale acetol is mainly obtained by catalytic oxidation starting from 1,2-propanediol (Chem. Eng. News 43 (1965)) or by dehydrogenation of 1,2-propanediol (DE 23 13 957 B).

However, a method that uses glycerol as starting material would also be of economic interest. The dehydration of glycerol at temperatures between 430 and 450°C is known ("Liebigs Annalen der Chemie," 1904, Vol. 335, pp. 209-223). In this case glycerol is slowly passed through a heated tube packed with pumice. For an input of 250 g glycerol the experiment takes roughly 16 hours. One obtains a good deal of graphite and a brown colored distillate that contains acetol, water, formaldehyde, acetaldehyde, acrolein, unreacted glycerol, and other substances. A fractional distillation is necessary to recover aqueous acetol or almost water-free acetal from the reaction mixture. Such a process is not suitable for industrial use. Only 73% of the input glycerol is converted and in the end the reaction mixture contains only 7.5% acetol, as can be taken from the figures given in that article. Moreover, the reaction progresses very slowly.

For this reason the invention is based on the task of improving the method mentioned above, so that it becomes industrially usable and allows considerably higher yields and conversions. The reaction mixture should contain mainly acetol and water and only insignificant amounts of byproducts.

This task is solved in accordance with the invention by the fact that glycerol is converted to acetol and water with a heterogeneous hydrogenation/dehydrogenation catalyst that contains an element of the 1st and/or 8th side groups of the Periodic Table at temperatures between 180 and 400°C.

The glycerol conversion is between 85 and 99.8% and the selectivity for acetol is surprisingly high, between 60 and 86%. Relatively high space-time yields are achieved. Propanediol is also formed as an intermediate product in minor quantities. Glycerol oligomers are not detectable. Also, the disadvantages of the known method that were cited above do not occur in accordance with the invention.

The conversions and selectivity are particularly high when water-free glycerol is used. Still better results are obtained if the glycerol that is used is diluted with a short-chain secondary alcohol, particularly isopropanol. This alcohol can easily be separated from the reaction mixture.

In particular, it was proposed that the reaction be carried out at temperatures between 240 and 300°C, especially at about 280°C.

Preferably, the catalyst contains copper, especially finely divided copper or copper oxide on a support. The use of copper chromite, copper zinc oxide, copper silicate, copper aluminum oxide or combinations thereof, possibly with promotors is also advantageous.

It is of interest from the economic standpoint that the method is carried out at pressures under 20 bar.

It is advantageous in particular for industrial use if the catalyst is in the form of a fixed bed. The liquid throughput per hour and volume of catalyst in this case is between 0.1 and 10 h^{-1}. The reaction temperature can be adjusted and controlled particularly readily when the process is carried out in a tubular reactor. However, it is also possible to use other types of reactors.

In another advantageous embodiment the unreacted glycerol and optionally the added short chain secondary alcohol are recycled to the feed product.

Embodiment examples of the invention are described in more detail below. The invention, however, is not limited to these examples.

Example 1

One liter of catalyst (type Cu chromite, 0203T, tablets 4 mm in diameter and thickness, product of the Engelhard Co.) were put into a thermal oil-heated steel reaction tube, dried, and reduced with 1% hydrogen in nitrogen at a temperature between 150°C and 200°C. Then the catalyst was heated to 260°C under a 0.5 m^3/h [STP] stream of nitrogen. 310 mL aqueous glycerol containing 80 wt% glycerol was fed by pump through a preheater at an LHSV of 0.25 h^{-1}. The experiment was "pressureless," i.e., carried out at atmospheric pressure. The resulting reaction mixture was cooled. The condensed components were collected in a separator.

The reaction contained, wt%: 13.5% unreacted glycerol, 30.1% acetol, 4.0% propanediol, 12.7% unidentified, water-soluble components and 34% water.

Example 2

The experiment was carried out as in Example 1. However, the heating was carried out to 280°C. The reaction mixture contained wt%: 7.2% unreacted glycerol, 36.4% acetol, 3.6% propanediol, 11.5% unidentified, water-soluble components and 35% water.

Example 3

The experiment was carried out as in Example 1. However, the feed was 1000 mL/h 80% aqueous glycerol. The analysis gave wt%: 9.9% unreacted glycerol, 24.8% acetol, 7.4% propanediol, 6.6% unidentified, water-soluble components and 38% water.

Example 4

This example was carried out under the same conditions as in Example 1 but heating was to 280°C and the feed was 1000 mL 80% glycerol. The analysis yielded 9.0% glycerol, 30.7% acetol, 4.8% propanediol, 8.7% unreacted components, and 38% water.

Example 5

This example was carried out under the same conditions as in Example 1 but heating was to 300°C and the feed was 310 mL 80% aqueous glycerol. The analysis yielded 0.3% glycerol, 18.5% acetol, 1.3% propanediol, 9.3% unreacted components, and 41.3% water.

Examples 6 to 11

These examples were carried out under otherwise the same conditions as in Example 1, using 99.5% glycerol and conducting the reactions at various temperatures and throughputs. The analysis results are summarized in Table 1.

Examples 12 to 14

These were carried out under otherwise the same conditions as in Example 1 except that 99.5% glycerol was diluted with isopropanol in an 80:20 weight ratio and the reactions were carried out at various temperatures and throughputs. The analysis results are given in Table 2.

[Claims only, as requested]

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METHOD OF PRODUCING ACETOL

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Claims

1. Method for the production of acetol by dehydration of glycerin at high temperatures, characterized by the fact that glycerin is reacted with a heterogenous hydration/dehydration catalyst containing an element of Subgroup 1 and/or 8 of the Periodic Table, at temperatures between 180-400°C to give acetol and water.

2. Method according to Claim 1, characterized by the fact that anhydrous glycerin is used.

3. Method according to Claim 1 or 2, characterized by the fact that the glycerin used is diluted with a short-chain, secondary alcohol, in particular, isopropanol.

4. Method according to one of Claims 1-3, characterized by the fact that the reaction is carried out at temperatures between 240-300°C, in particular, at approximately 280°C.

5. Method according to one of Claims 1-4, characterized by the fact that the catalyst contains copper, in particular, copper or copper oxide finely distributed on a carrier.

6. Method according to one of Claims 1-5, characterized by the fact that it is carried out at pressures less than 20 bar.

7. Method according to one of Claims 1-6, characterized by the fact that the catalyst is present as a fixed bed and the liquid throughput per hour and catalyst volume is between 0.1-10 h^{-1}.

8. Method according to one of Claims 1-7, characterized by the fact that unconverted glycerin and possibly the added short-chain, secondary alcohol are recycled as input products.